Energy Photovoltaics, Inc.
276 Bakers Basin Road
Lawrenceville, NJ 08648

December 14, 2004

Dr. Harin Ullal, Technical Monitor
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

Dear Harin,

This is the fourth quarterly report for Phase III for EPV's cost-shared subcontract RDJ-2-30630-21 **Advanced CIGS Photovoltaic Technology** awarded under the Thin Film Photovoltaics Partnership Program. The nominal period covered by the report is 9/1/04 – 11/30/04. As the result of a no-cost extension, work under the subcontract will continue through February 13, 2005.

During this period the core CIGS group consisted of Dr. Alan Delahoy, Dr. Leon Chen, Dr. Baosheng Sang, Dr. Masud Akhtar, John Cambridge, Frank Ziobro, Ramesh Govindarajan, and Renata Saramak.

This letter summarizes activities conducted in this quarter. The main areas concerned:

1) CIGS absorber and device optimization
2) Cu selenization experiments
3) Front and back contacts
4) Surface treatment and annealing
5) Background work for sub-micron device and module
6) Hercules sources
7) Equipment and measurement
8) Characterization performed externally
9) Conference papers and other news

1) CIGS absorber and device optimization

We continued efforts to optimize our hybrid CIGS process during this quarter. In an attempt to boost device Voc, several variables were explored. Among them, the sensitivity of Voc to the Ga ratio in the third stage was tested. While we did find that Voc increased with higher Ga ratio in that stage, the change was less impressive than expected. At the same time, we observed that device FF deteriorated. Further systematic experiments are planned for the next quarter.

In addition to focusing on the junction, we also investigated CIGS bulk properties such as activation energy. The logarithm of conductivity showed a very nice linear trend vs. reciprocal of temperature in the temperature range 30°C to 100°C. But, a surprisingly high activation energy of 0.36 eV concerns us. If real, that could in part explain the unexceptional Voc found in our devices. On the other hand, it might not be related to device performance since what we measured is lateral conductivity rather than vertical. We plan to correlate device Voc and activation energy in a number of samples to see if lateral activation energy (a material property) is a useful predictor of device performance.

By accident, we made a device having a very thick i-ZnO layer of about 1 μm. To our surprise, the device performed well with only slightly lower Jsc, comparable FF, and even a little better Voc than in normal devices. A QE curve showed depressed short wavelength response due to ZnO band edge absorption, while the long wavelength response was hardly affected at all due to lack of free carrier absorption in the i-ZnO layer. However, it is still not clear to us why FF and series resistance suffered so little. Similar experiments were deliberately repeated a couple of times, and the results were very similar.

The best performance of devices produced in our large deposition system (Zeus) in this period was 12.7% efficiency (Voc 543 mV, FF 70.1% and Jsc 33.4 mA/cm^2). With a metal grid and AR coating these devices would likely reach 14%. A SEM picture of a sample cut from the same big plate is printed in Fig. 1. Large, well-formed grains with a clear columnar structure are evident. The origin, and possible electrical effect, of the horizontal interface in the middle of the CIGS layer is not clear and warrants further investigation.

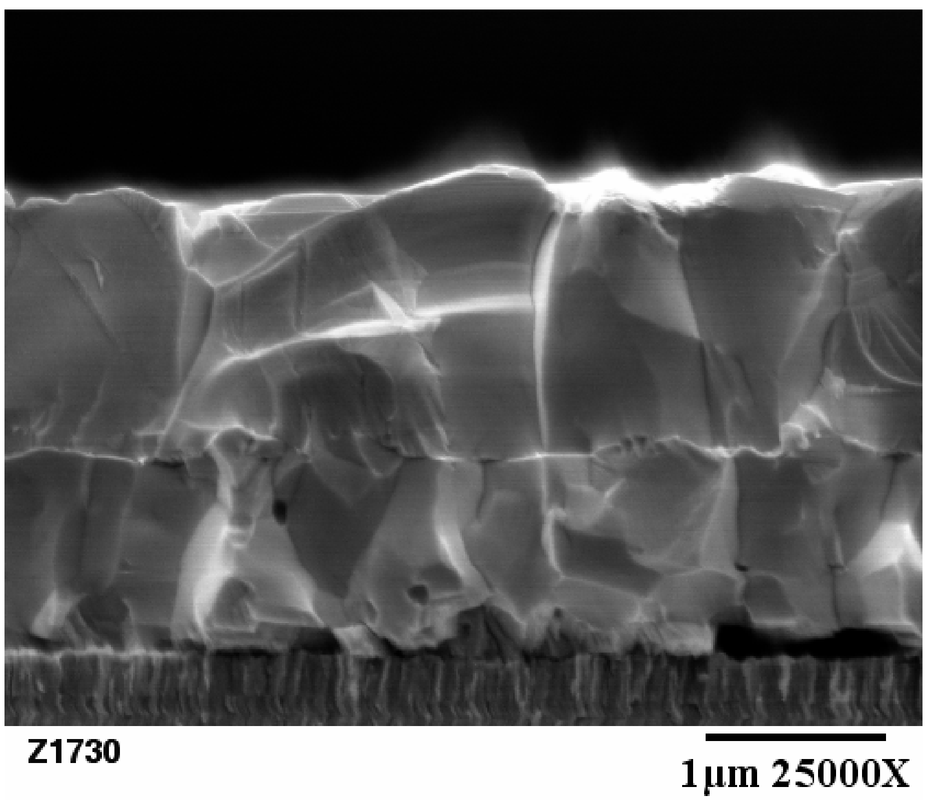


Fig. 1. SEM cross section of CIGS from run Z1730 (micrograph courtesy NREL).

2) Cu selenization experiments

The selenization of Cu in a Se environment, which is possibly relevant to our hybrid process, was studied in our research system (Hercules). We found that Cu is very easy to selenize at elevated temperatures. The resistivity of a fully selenized copper film with Se/Cu ratio 0.5 was found to be about ten times larger than that of the copper film before selenization. Therefore, film resistivity is a good indicator of selenization. No selenization was detected at room temperature, but it does start at temperatures as low as 50°C. This information could provide an additional process variable in our optimization of the CIGS absorber.

3) Front and back contacts

We have not been satisfied with the new $ZnO:Al_2O_3$ target supplied by a new vendor. The optical and electrical properties of the resulting ZnO:Al TCO films were apparently worse than those obtained with our old target obtained from a different vendor. In addition, the ZnO interconnection line often peeled off from the Mo to cause series resistance in modules. In an effort to improve the ZnO, magnets in the ZnO cathode were redesigned and replaced with a new set of magnets. A new field pattern was observed, as demonstrated in Figures 2 and 3. Interestingly enough, for films of equal sheet resistance, the optical absorption is now reduced. However, we are still fighting the ZnO interconnection peeling in the module process. This might result not only from stress in the ZnO film but also from an insufficiently clean Mo surface. We will return to this issue in section 7).

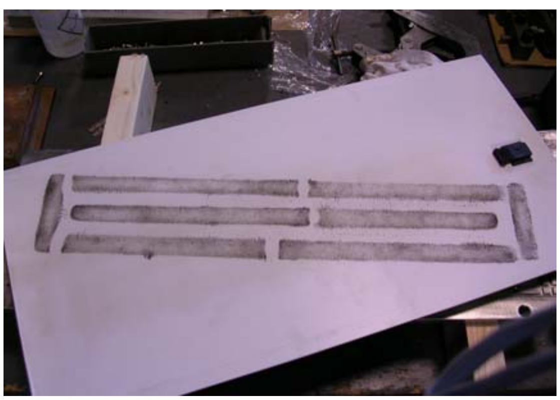


Fig. 2. Magnetic field traced by iron filings in old configuration.

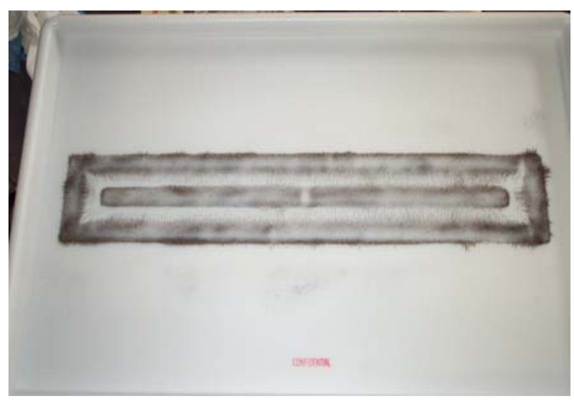


Fig. 3. Magnetic field traced by iron filings in new configuration.

In another effort related to the front TCO, we have produced boron-doped ZnO films by reactive environment, hollow cathode sputtering, and applied these films to devices. The results are encouraging. An efficiency of 11.5% was achieved using HC n-ZnO:B, as shown in the Table below. Time permitting, further CIGS devices will be processed with window layers produced by RE-HCS (such as ZnO:B or In_2O_3:Ti) in the coming quarter.

Structure CIGS/...	V_{oc} mV	J_{sc} mA/cm^2	FF %	Eff %
CdS/i-ZnO(RF)/ZnO:B(HC)	588	28.4	69.0	11.5
CdS/i-ZnO/In_2O_3:Ti*	565	28.4	66.8	10.7

*reported in quarterly #2

With regard to the back contact, a few new directions and ideas were pursued and tested. Some of this work was motivated by the recent upsurge in interest in CIGS layers of sub-micron thickness. Firstly, a Mo layer with half the thickness of our usual one was deposited on a textured CTO glass substrate. In view of the fact that light trapping is desirably incorporated in a sub-micron CIGS absorber to help compensate for current loss in the thinner absorber, depositing the CIGS layer on a textured substrate might help. As a first step, we wanted to find out if such a device performed reasonably well. We were pleased to observe a device FF of 72% using such a structure. This was higher than that of a normal reference back contact in the same run. A second run confirmed the observation. However, no current increase was observed. Secondly, to enhance back contact reflectivity, which again is important for sub-micron absorbers, TiN films were coated on Mo/glass in the HC system. A noticeable improvement of reflectivity in the long wavelength region was found. These 1”x1” substrates were sent to the Institute of Energy Conversion at the University of Delaware for CIGS deposition and device processing. An 11.7% cell was achieved, which is an encouraging figure for such preliminary work. Thirdly, we are evaluating Mo films on glass supplied by a commercial glass coater. A first test run using this Mo yielded a device performance of 12%, the same level as achieved using EPV Mo. Further Mo films prepared under slightly different process conditions have been received for evaluation.

4) Surface treatment and annealing

In addition to our standard post-CIGS treatment, we are exploring new materials and ways to treat the CIGS surface. Some results are quite encouraging, as device performance in test samples is very similar to that obtained using our standard treatment. Further investigations will focus on performance improvement and process simplification. In collaboration with other organizations, some CIGS samples have been sent to U. Florida and InterPhases Research for buffer layer and surface engineering experiments.

Many annealing experiments such as post-CIGS, post-CdS, and post-ZnO have been tested thoroughly at EPV. In many cases, post-CdS annealing showed either better device performance or more robust and consistent performance, especially for ZnO deposited by RF sputtering where the samples are not heated deliberately. Therefore, we have adopted it as a standard step for devices processed this way. For module production in the in-line sputtering system, the annealing step is not used.

5) Background work for sub-micron device and module

A certain amount of background work was devoted to the issue of CIGS devices and modules having a sub-micron thick absorber layer in this quarter. Reduction of indium consumption, and by implication, of CIGS layer thickness, could become a critical issue for future large scale CIGS module production due to the limited availability of indium. We were also encouraged by exciting news from NREL that a device efficiency of 16% was achieved with only a 1 μm thick CIGS absorber layer.

The following is a list of some of the things we have done or are doing:

- The published literature was surveyed.
- A potential collaboration and agreement with IEC was established.
- The absorption of CIGS at various band gaps was used to calculate Jsc for a wide range of CIGS thickness down to 0.4 µm. The maximum current available as a function of band gap for a AM1.5 global spectrum is plotted in Fig. 4.

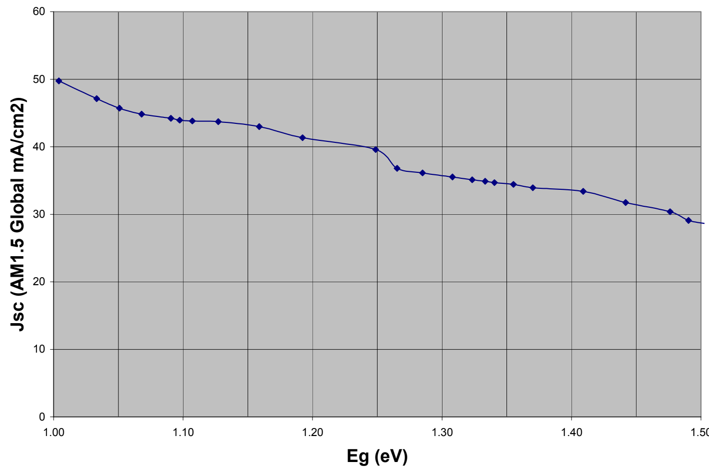


Fig. 4. Maximum current density available under AM1.5 global spectrum.

- Some ideas for potentially light trapping structures were tested in preliminary fashion, see section 3) above.
- CIGS devices were deposited on alternative back contacts, see section 3).
- Device performance including efficiency, Voc, FF and Jsc for various band gaps and absorber layer thicknesses was modeled with AMPS in collaboration with University of Florida (Jiyon Song). Some results are plotted in Fig. 5.
- The first devices and module having a sub-micron (0.85 µm) CIGS absorber layer were produced in our production chamber Zeus. A best device efficiency of 8.9% and module efficiency of 3.8% (7W, area 1850 cm^2) were measured. No obvious shunting behavior was found in the devices. The module has not yet been fully analyzed.

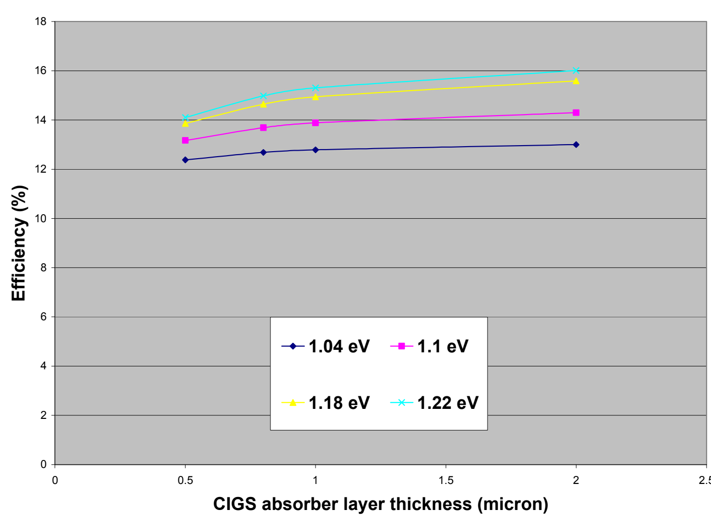
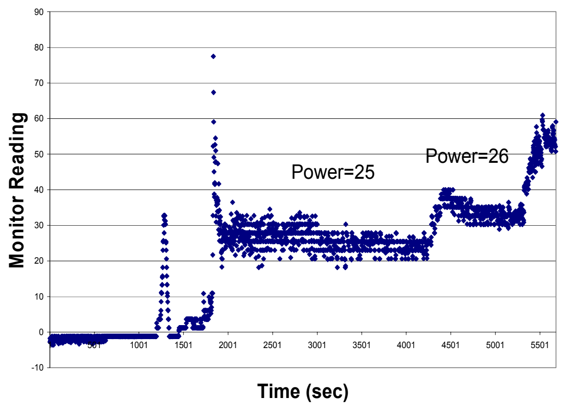
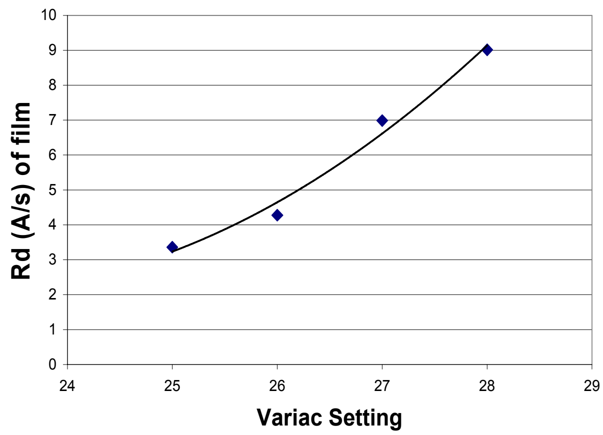


Fig. 5. Device efficiency as a function of absorber thickness (bandgap as parameter).

6) Hercules sources

The evaporation sources used for In, Ga and Cu in the R&D Hercules system are open boats controlled by Variac transformers and monitored using an Inficon crystal thickness monitor. Deposition rate is far from constant even at a constant power setting. Manual adjustment of the power levels to control deposition rates is challenging for simultaneous evaporation from multiple sources. A crucible configuration to replace the open boats was tested in this quarter. Calibration runs with two materials, pure copper and in-house IGS compound, were performed at a constant power setting. We found the Cu deposition rate failed to settle down to a stable value even after 10 minutes, while the IGS quickly reached a constant rate at a given power level. Plotted in Fig. 6A is the IGS deposition rate vs. time for a series of power settings, while Fig. 6B shows calibration of real deposition rate vs. power setting. A further possibility is to utilize effusion sources (Knudsen cells).





7) Equipment and measurement

We have already mentioned the recent peeling problem at scribe #2. It appears partly due to the Mo surface that results from washing in the Bilco glass washer in the a-Si manufacturing line. For better control of the quality of glass cleaning before Mo deposition and cleaning of the Mo surface and gap after laser scribing the Mo, an order for an ultrasonic tank large enough for CIGS modules was placed. It should be received by the end of the year. It is hoped that this will be helpful in improving process control for the module production line.

The entry of pump oil into the sputter chamber of our ILS was encountered during this quarter. The root cause was a leaky diffusion pump gate valve in the entry chamber. This allowed air to enter a common fore-line when the entry chamber was vented, causing oil to enter the process chamber. Thorough cleaning of the ILS was performed and separation of the fore-lines is planned.

A small portable IV station run by a lap-top computer for measurement of dot-type devices outdoors was recently set up. The intent is to allow more accurate I-V curves and current density measurement under the real sun spectrum.

8) Characterization performed externally

At the end of this period SEM and Auger analyses were performed at NREL (To and Pankow), and X-ray diffraction was performed at IEC, U. Delaware (McCandless). The data will be reported and discussed in the Final Report.

9) Conference papers and other news

EPV presented three technical papers at the DOE Solar Energy Technologies Review Meeting held in Denver, CO, October 25-28, 2004. Regarding this subcontract, Dr. Alan Delahoy, in a paper entitled "Large Area CIGS Films and Modules Produced by a Hybrid Process, and High Performance TCOs," reported the production of solar cells with efficiencies greater than 13% (as verified by NREL) made on CIGS films produced in EPV's pilot line system, and of transparent conducting oxides that set a record for the electron mobility in such materials made by sputtering techniques.

EPV also presented a paper at the 51st American Vacuum Society Meeting held in Anaheim, CA during November 14-19, 2004. Dr. Sheyu Guo, in a paper entitled "Transparent and Semi-Transparent Conducting Film Deposition by Reactive-Environment, Hollow Cathode Sputtering" described EPV's RE-HCS technology with application to indium oxide, zinc oxide, and indium nitride. For more information see www.epv.net.

EPV will be presenting four papers at the 31st IEEE PVSC in January 2005, one of them on CIGS.

Recent publication: Alan E. Delahoy, Liangfan Chen, Masud Akhtar, Baosheng Sang, Sheyu Guo "New Technologies for CIGS Photovoltaics" *Solar Energy* 77 (2004) 785-793.

On the commercial side, EPV has been asked to provide a quotation for doubling the capacity of the a-Si plant in Tianjin, China. EPV is also receiving increased demand from Germany for its dual-junction a-Si modules.

Sincerely,

Alan E. Delahoy	Leon Chen
Principal Investigator	Senior Scientist